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ANNUAL REPORT TO THE U.S. ATOMIC ENERGY COMMISSION

by

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## I. INTRODUCTION

The importance of fundamental research in the solid state sciences is well recognized. This is a branch of Materials Science and Engineering which has been of great significance in regard to both the civilian and military segments of the national economy. The past decades have given many examples in which the technology necessary to our national interest has drawn heavily upon the results of basic research. This is true especially in the field of metallurgy.

During the past few years we have been investigating the electronic characteristics of metal systems as they are reflected in the specific heats at low temperatures and in the magnetic behavior. We have attempted, wherever possible, to relate the results of our measurements to the crystallographic and structural characteristics of the systems. The long-range purpose of this work has been the gathering of information which will help to advance our understanding of the behavior of metal systems. The work reported here was directed toward this same goal. Principal emphasis has been laid on systems containing the lanthanide, or rare earth, elements since (1) these systems have not been extensively investigated, and (2) they give promise of shedding light on the more complex and industrially more significant systems containing d-transition metals and the actinides.

## II. RESUME OF WORK TO DATE

### A. Published Work Since Inception of the Program

Prior to September 1, 1964, the authors of this report were involved with two contracts with the U.S. Atomic Energy Commission - Contract No. AT(30-1)647 with W.E. Wallace as Principal Investigator and Contract No. AT(30-1)2163 with R.S. Craig as Principal Investigator. As these programs had similar objectives and used similar facilities, it was decided to combine them into one program with the authors as co-Principal Investigators. Thus, in a legal sense, on September 1, 1964, a new contract began. However, in a scientific sense this represented continuation of earlier effort. To give some idea of the activity in and scope of the entire program since its inception a list of papers originating in the work is given in Appendix I.

### B. Results Obtained in the Preceding Twelve-Month Period

#### (1) List of Papers Published, Accepted for Publication or Submitted for Publication:

1. W.E. Wallace, "Magnetism in Intermetallic Compounds," Progress in Solid State Chemistry, Vol. 6, 155 (1971).
2. R.D. Hutchens, V.U.S. Rao, J.E. Greedan, W.E. Wallace and R.S. Craig, "Magnetic and Electrical Characteristics of  $\text{REPd}_3$  Intermetallic Compounds," J. Appl. Phys. 42, 1293 (1971).
3. B. Leon, V.U.S. Rao and W.E. Wallace, "Magnetic Characteristics of the Aluminum-rich Ternary Laves Phases Containing Rare Earths, Nickel and Aluminum," J. Less Common Metals 24, 247 (1971).
4. W.M. Swift and W.E. Wallace, "Reversal of Coupling in Intermetallic Compounds Containing Two Rare Earth Elements," J. Solid State Chem. 3, 180 (1971).

5. R.D. Hutchens and W.E. Wallace, "Magnetic Properties of Rare Earth-Lead Intermetallics," *J. Solid State Chem.* 3, 564 (1971).
6. S. Nasu, H.H. Neumann, N. Marzouk, R.S. Craig and W.E. Wallace, "Specific Heats of  $\text{LaNi}_5$ ,  $\text{CeNi}_5$ ,  $\text{PrNi}_5$ ,  $\text{NdNi}_5$  and  $\text{GdNi}_5$  Between 1.6 and 4°K," *J. Phys. Chem. Solids* 32, 2779 (1971).
7. H.H. Neumann, S. Nasu, R.S. Craig, N. Marzouk and W.E. Wallace, "Specific Heats of  $\text{LaNi}_2$  and  $\text{NdNi}_2$ ," *J. Phys. Chem. Solids* 32, 2788 (1971).
8. S. Nasu, A.M. Van Diepen, H.H. Neumann and R.S. Craig, "Specific Heats of  $\text{LaIn}_3$ ,  $\text{CeIn}_3$  and  $\text{PrIn}_3$  at Temperatures Between 1.5 and 4.2°K," *J. Phys. Chem. Solids* 32, 2773 (1971).
9. W.E. Wallace, T.V. Volkmann and H.P. Hopkins, Jr., "Magnetic Characteristics of Some Ternary Intermetallic Compounds Containing Lanthanides," *J. Solid State Chem.* 3, 510 (1971).
10. V.U.S. Rao, R.D. Hutchens and J.E. Greedan, "Influence of the Crystalline Electric Field on the Kondo Resistivity of  $\text{Ce La}_x \text{Pd}_{3-1-x}$  Ternaries," *J. Phys. Chem. Solids* 32, 2755 (1971).
11. R.D. Hutchens, V.U.S. Rao, J.E. Greedan and R.S. Craig, "Electronic Specific Heat of  $\text{Ce La}_x \text{Pd}_{3-1-x}$  Ternary Alloys," *J. Phys. Soc. Japan* 32, 451 (1972).
12. H.J. Schaller, R.S. Craig and W.E. Wallace, "Magnetic and Crystallographic Characteristics of Solid Solutions of Gd in Pd and Pd-Ag Alloys," *J. Solid State Chem.*
13. W.E. Wallace, "Magnetic Properties of Rare Earth Hydrides," *Ber. Bunsenges, Physik Chem.*
14. C.G. Titcomb, R.S. Craig, W.E. Wallace and V.U.S. Rao, "Effect of Hydrogen on the Electrical and Magnetic Behavior of  $\text{PrCo}_2$  and  $\text{NdCo}_2$ ," *Phys. Letters*.
15. E. Segal and W.E. Wallace, "Rare Earth Ions in a Hexagonal Field, II," *J. Solid State Chem.*
16. C.G. Titcomb and W.E. Wallace, "Equilibrium Pressures of the Hydrogen-Niobium System as a Secondary Standard for Ultrahigh Vacuum Gauge Calibration," *J. Vac. Science and Technology*

(2) Completed Work - In Preparation

1. S. Nasu, R.S. Craig, W.E. Wallace, H.H. Neumann and N. Marzouk, "Specific Heat of  $CeCo_2$  at Temperatures Between 1.6 and 300°K."
2. R.D. Hutchens and W.E. Wallace, "Magnetic Characteristics of Lanthanide-Indium ( $Ln_3In$ ) Intermetallics."

(3) Summary of Completed Work

The reprints and preprints, which are available upon request, give a complete account of the work cited in (1). A brief account of the studies listed in (2) is now provided.

Specific Heat of  $CeCo_2$  Between 1.6 and 300°K  
(work of S. Nasu, H.H. Neumann and N. Marzouk)

Heat capacities of  $CeCo_2$  have been measured in the ranges 1.6 to 4.1°K and 8 to 300°K. Results in the liquid helium range showed a marked deviation from the usual relation  $C/T = \gamma + \beta T^2$ , giving a minimum at  $T^2 \approx 6^\circ K^2$  when  $C/T$  is plotted against  $T^2$ .  $\gamma$  was determined to be 14.5 mj. deg.<sup>-2</sup> g. atom<sup>-1</sup> by fitting data to an equation of the form  $C/T = \gamma + \beta T^2 + 2bT^2 \ln T/T_2$ , suggested by the work of Doniach and Engelsberg.<sup>1</sup> An electron-phonon enhancement factor of 0.68 was determined. Near room temperature the heat capacity is large, exceeding the Dulong-Petit limit. The origin of the large heat capacity is obscure. Results for  $CeCo_2$  and  $CeNi_2$  are very similar in all respects, indicating that the anomalous behavior probably originates with the cerium component of these compounds.

<sup>1</sup>S. Doniach and S. Engelsberg, Phys. Rev. Letters 17, 1750 (1966).

*will be published*



Magnetic Characteristics of  $\text{Ln}_3\text{In}$  Compounds  
(work of R.D. Hutchens)

The study of the rare-earth intermetallics forming with indium has been limited in the past to the series  $\text{LnIn}_3$ .<sup>2</sup> Crystallographically these compounds exhibited the  $\text{Cu}_3\text{Au}$  f.c.c. structure and magnetically there was a tendency for antiferromagnetic order. It was thought that the  $\text{Ln}_3\text{In}$  compounds could be logically investigated next. Although the crystal structure was not known for the whole series, at least one compound,  $\text{Pr}_3\text{In}$ , was known to have a f.c.c. structure similar to that of  $\text{LnIn}_3$ .<sup>3</sup>

These compounds were prepared by induction melting in MgO crucibles. X-ray diffraction patterns indicated that the samples were single phase at least in the case of the light rare earth compounds investigated (Pr, Nd). These compounds were indexed as f.c.c. structures.\* The lattice parameters are given in Table I. There appeared to be a structural change at  $\text{Gd}_3\text{In}$ . The heavy rare earth investigated (Gd, Dy, Er) could not be indexed as cubic structures. The patterns were simple when compared to those expected for orthorhombic or hexagonal structures, in which rare earth intermetallics are frequently found to form. The conclusion was that the structure was some type of distortion of cubic symmetry, but further investigation of this point did not seem fruitful enough to justify the expenditure of more time on the problem.

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<sup>2</sup>K.H.J. Buschow, H.W. de Wijn and A.M. Van Diepen, J. Chem. Phys. 50, 137 (1969).

<sup>3</sup>A. Iandelli, Atti Accad. Nazl. Lincei. Rend. Classe Sci Fis. Mat. Nat. 2, 327 (1947).

\*Superlattice lines, which would be expected in an ordered  $\text{Cu}_3\text{Au}$  structure, were not detectable in these compounds because of the near equality of the scattering factors of the constituent atoms.

TABLE I

Lattice Parameters for the  $\text{In}_3\text{In}$  System

Compound	$a_0$ ( $\text{\AA} \pm .01 \text{\AA}$ )
$\text{Pr}_3\text{In}$	4.90
$\text{Nd}_3\text{In}$	4.93

The magnetic results are tabulated in Table II. The results for  $\text{Pr}_3\text{In}$  and  $\text{Nd}_3\text{In}$ , shown in Figs. 1-6, indicate ferromagnetic ordering with Curie temperatures at  $62^\circ\text{K}$  and  $114^\circ\text{K}$  respectively. Tendency toward saturation is clearly evident (Figs. 3 and 6) at 20 kOe, the highest field employed.

Fig. 7 shows the thermomagnetic results for  $\text{Gd}_3\text{In}$ . The three curves of the figure demonstrate the peculiar magnetic behavior of this compound. At 18 kOe the magnetization-temperature behavior of this compound is characteristic of a ferromagnetically ordered material with a fairly high Curie point,  $213^\circ\text{K}$ . At lower fields of 5.3 kOe and 1.1 kOe maxima are seen in the magnetization versus temperature curves at  $81^\circ\text{K}$  and  $112^\circ\text{K}$ . This behavior is also depicted in the magnetization versus field strength data given in Fig. 8. The magnetic behavior of  $\text{Gd}_3\text{In}$  is indicative of metamagnetism for this material.

Figs. 9 and 10 show the thermomagnetic data of  $\text{Dy}_3\text{In}$  and  $\text{Er}_3\text{In}$  with Curie points indicated at  $138^\circ\text{K}$  and  $51^\circ\text{K}$  respectively. The magnetization versus field results in Fig. 11 give no evidence for metamagnetic behavior as was the case in  $\text{Gd}_3\text{In}$ .

In all six samples, the effective moments calculated from the  $\chi_M^{-1}$  vs T plots were within experimental error of those calculated for the free ions.

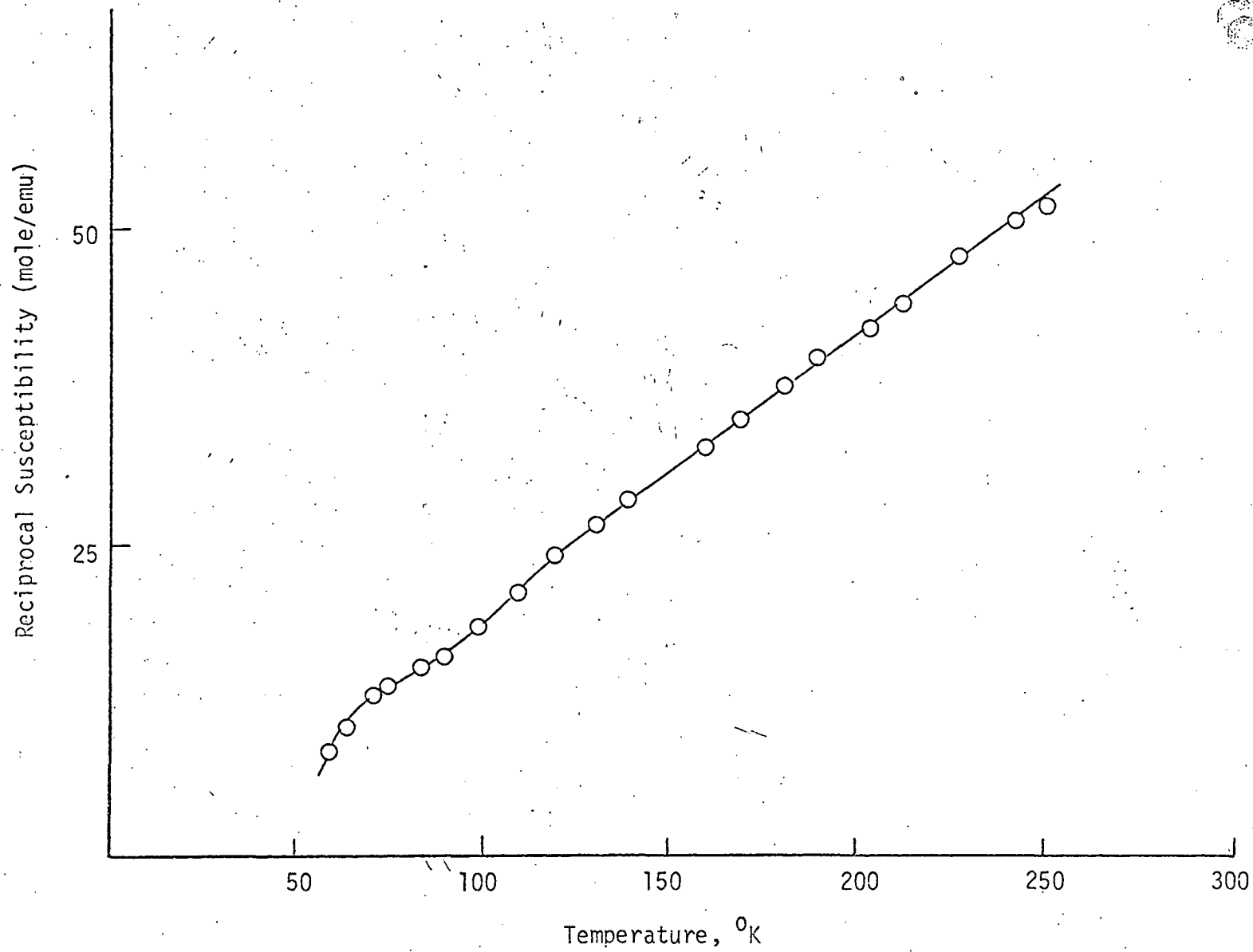


Figure 1 Reciprocal Susceptibility versus Temperature,  $\text{Pr}_3\text{In}$

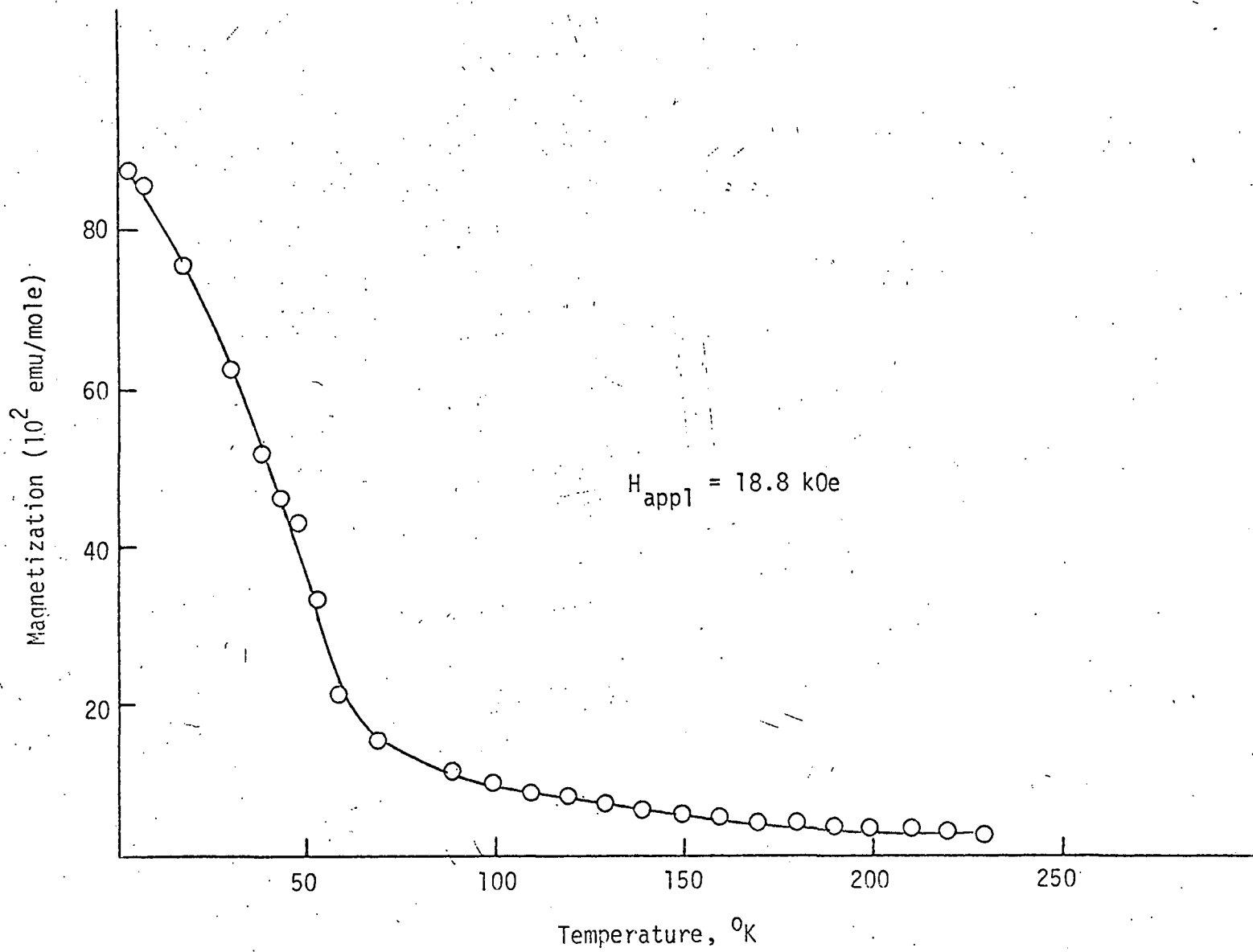


Figure 2 Magnetization versus Temperature,  $\text{Pr}_3\text{In}$

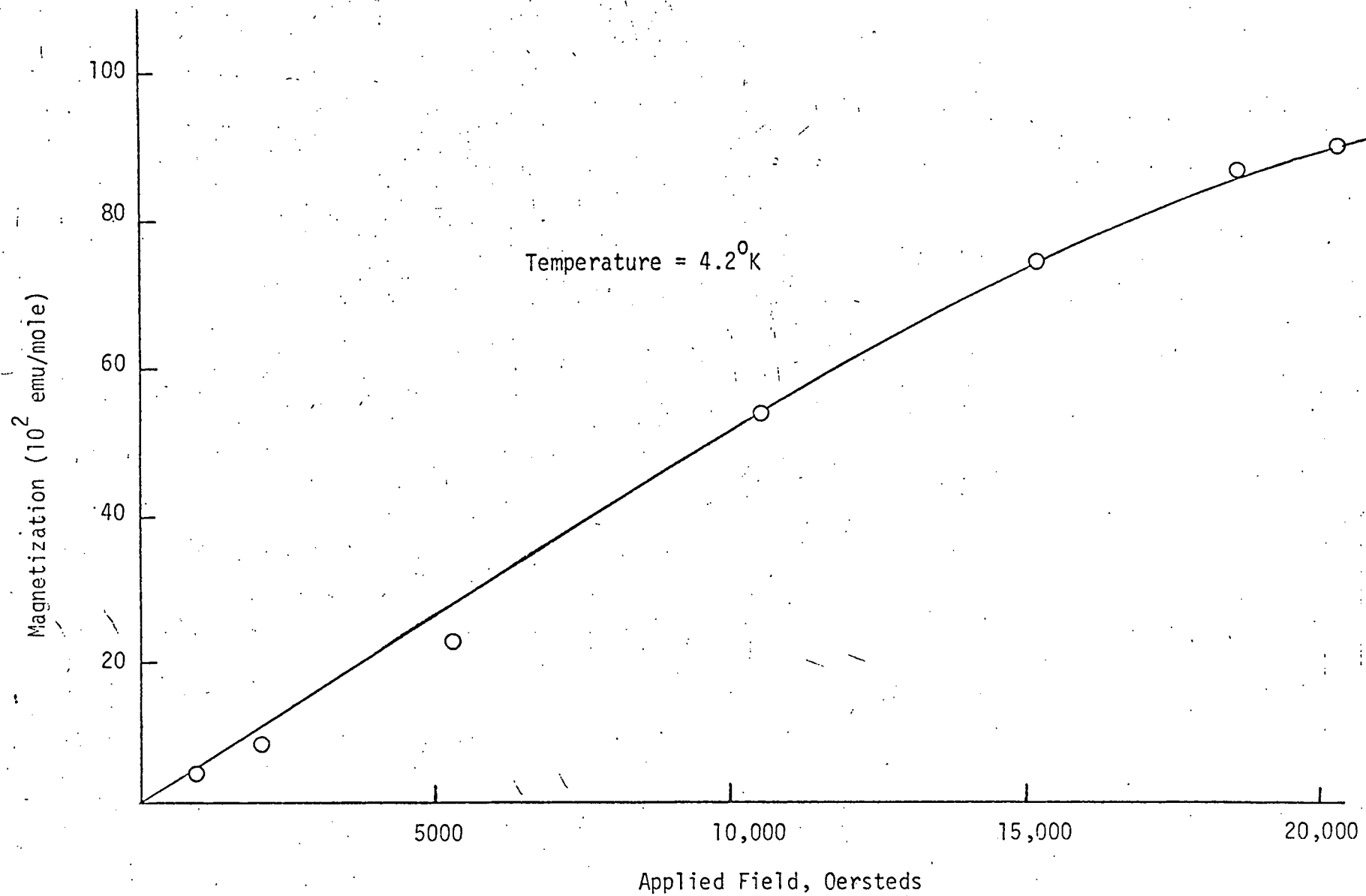


Figure 3 Magnetization versus Applied Field,  $\text{Pr}_3\text{In}$

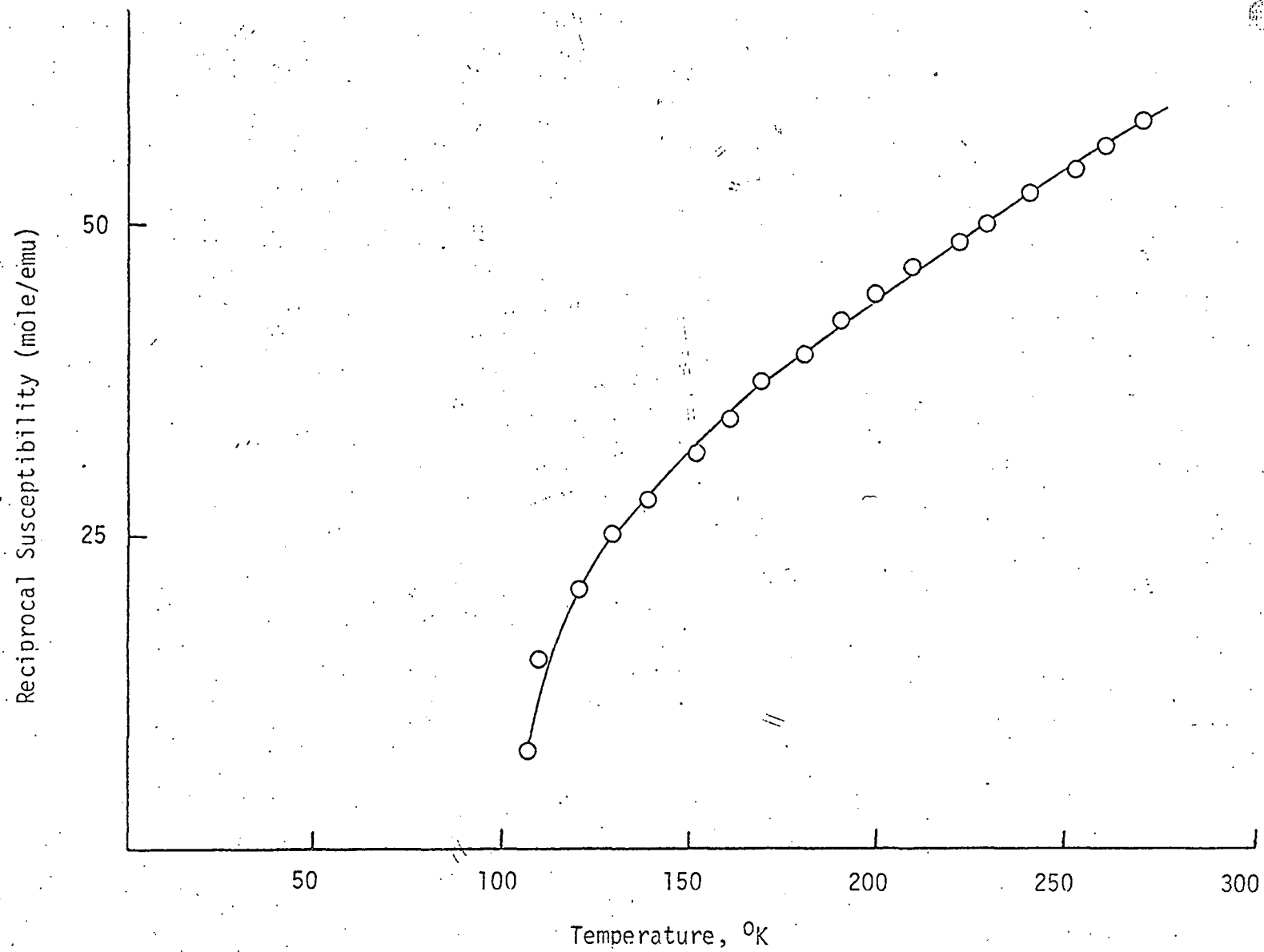


Figure 4 Reciprocal Susceptibility versus Temperature,  $\text{Nd}_3\text{In}$

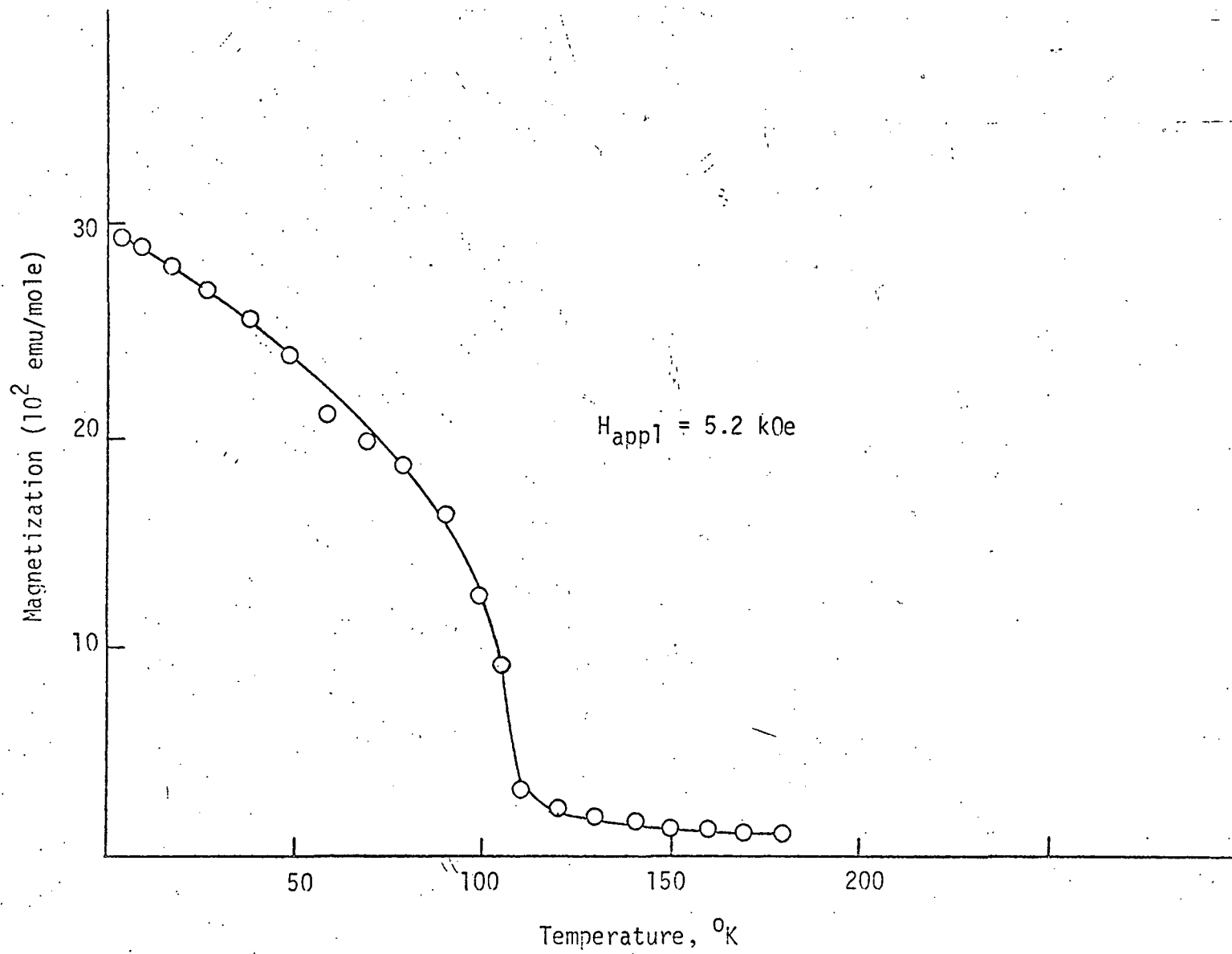


Figure 5 Magnetization versus Temperature,  $\text{Nd}_3\text{In}$

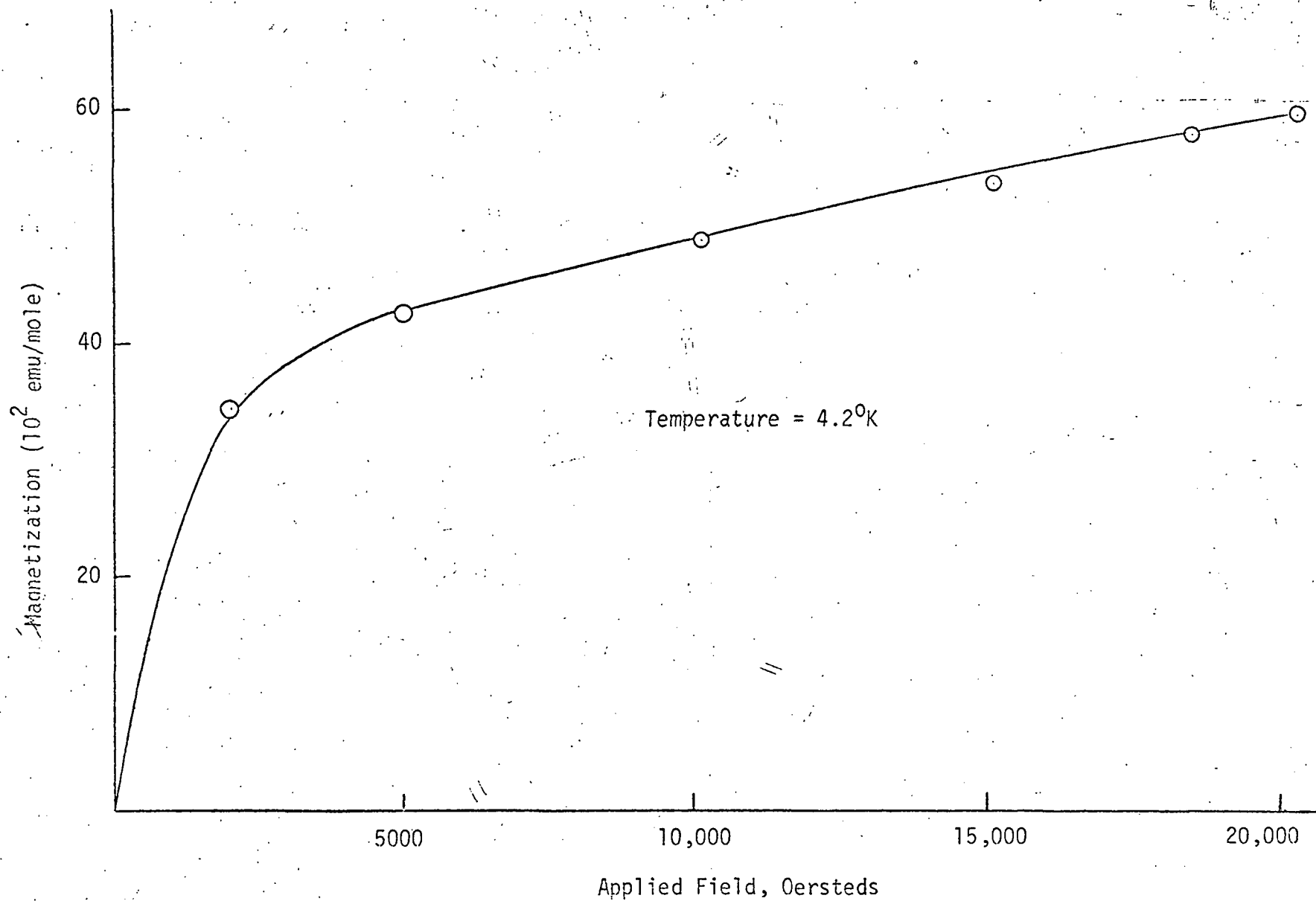


Figure 6 Magnetization versus Applied Field, Nd<sub>3</sub>In



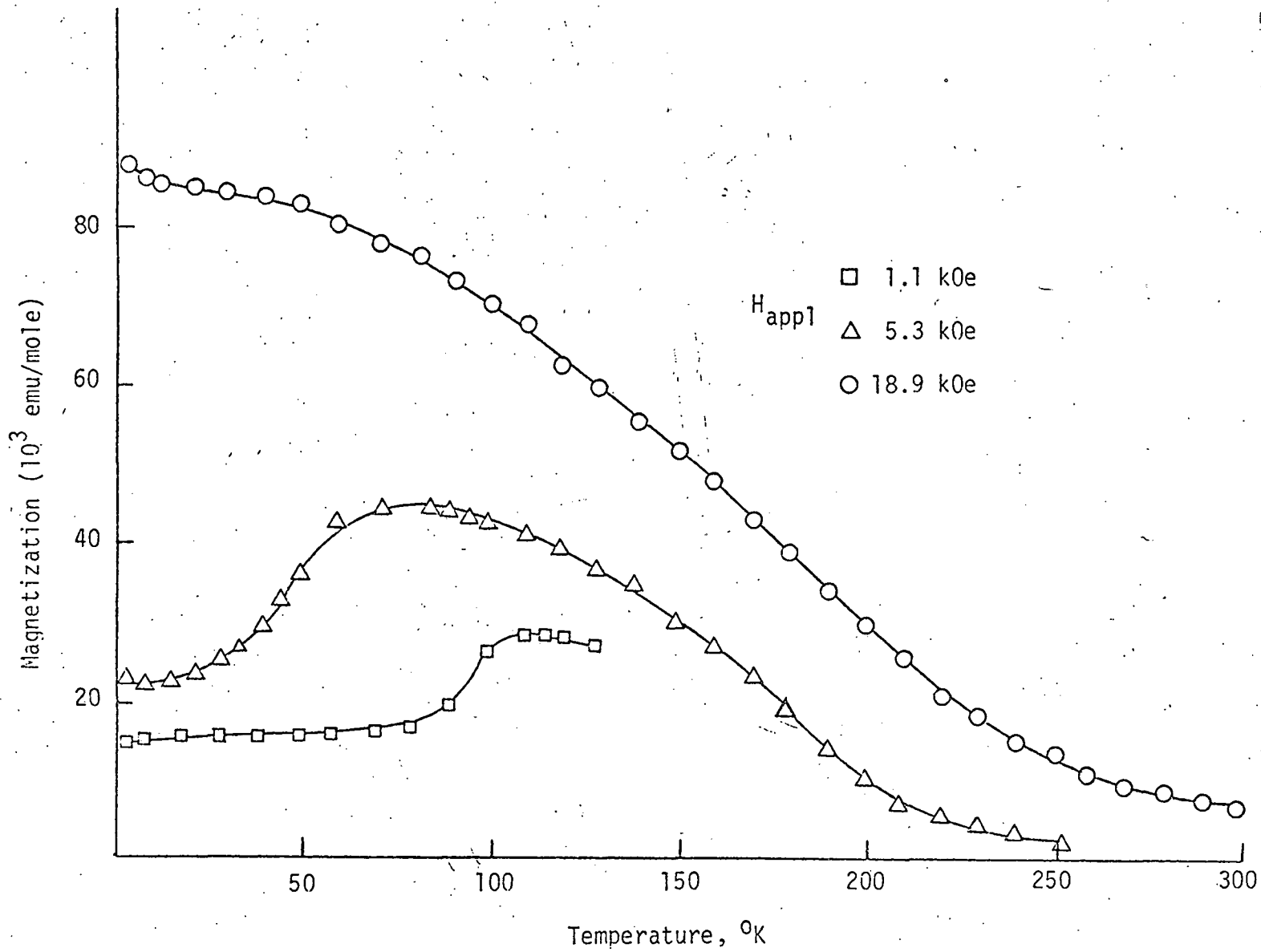


Figure 7 Magnetization versus Temperature, Gd<sub>3</sub>In

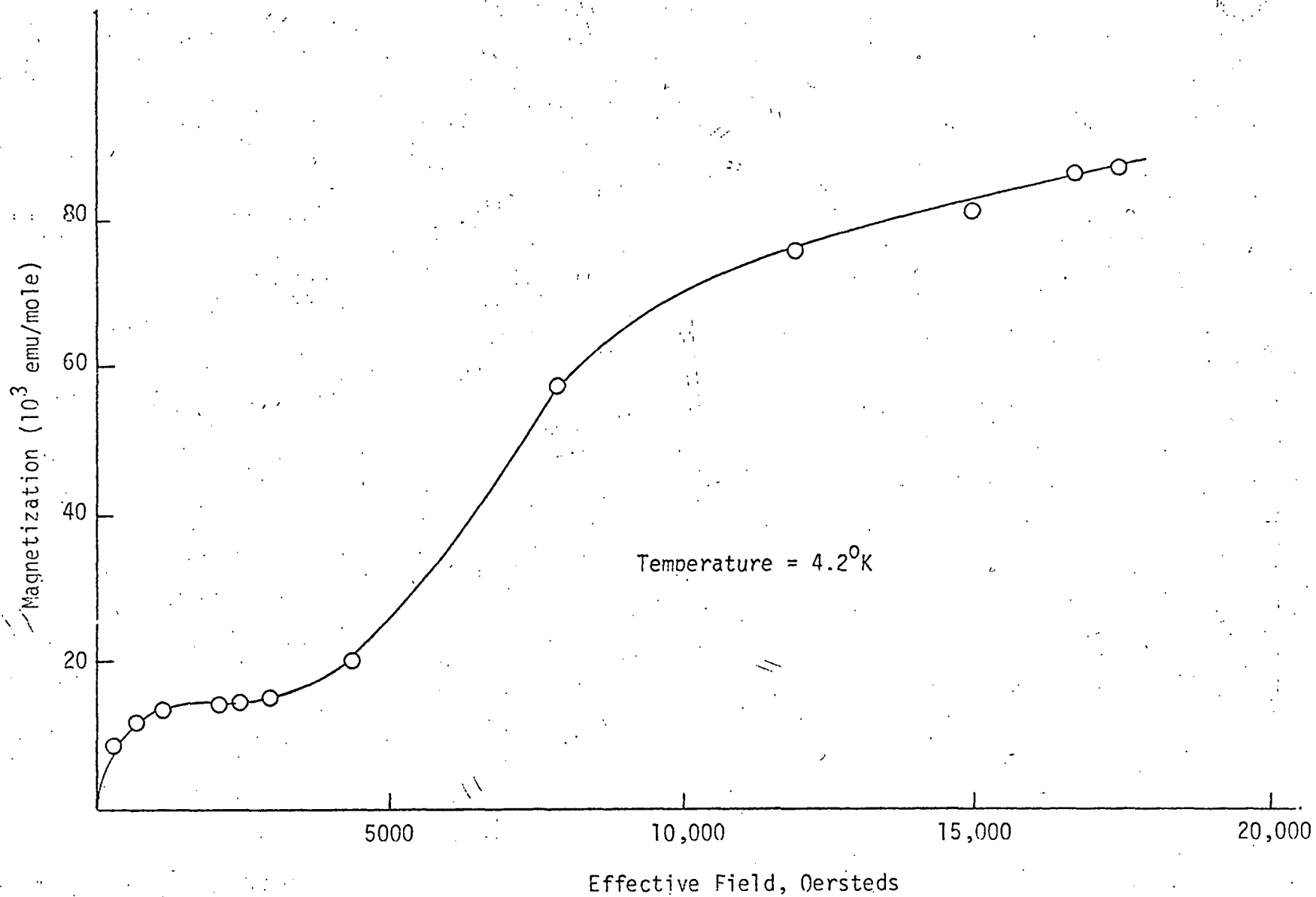


Figure 8. Magnetization versus Effective Field, Gd<sub>3</sub>In

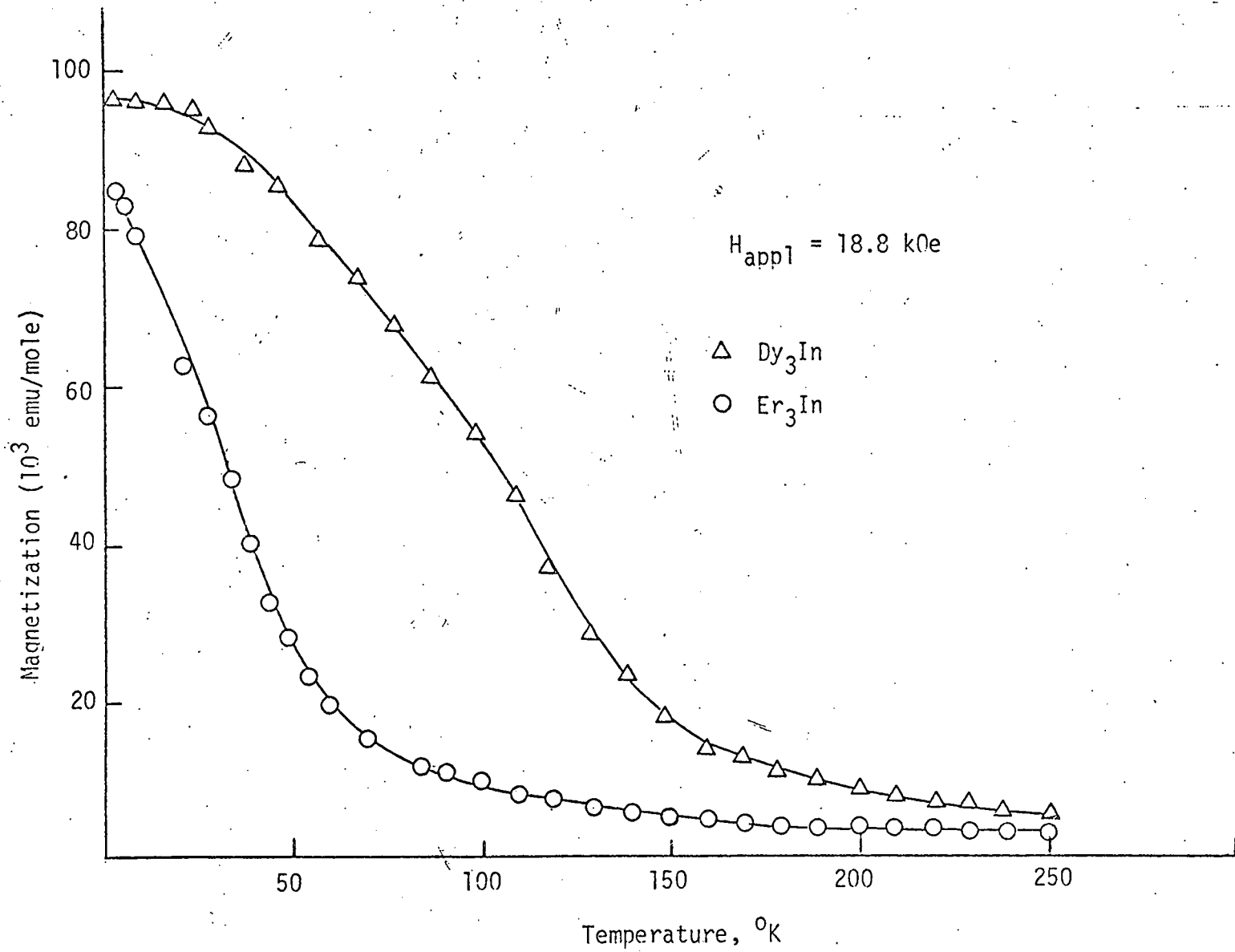


Figure 9 Magnetization versus Temperature, Dy<sub>3</sub>In and Er<sub>3</sub>In

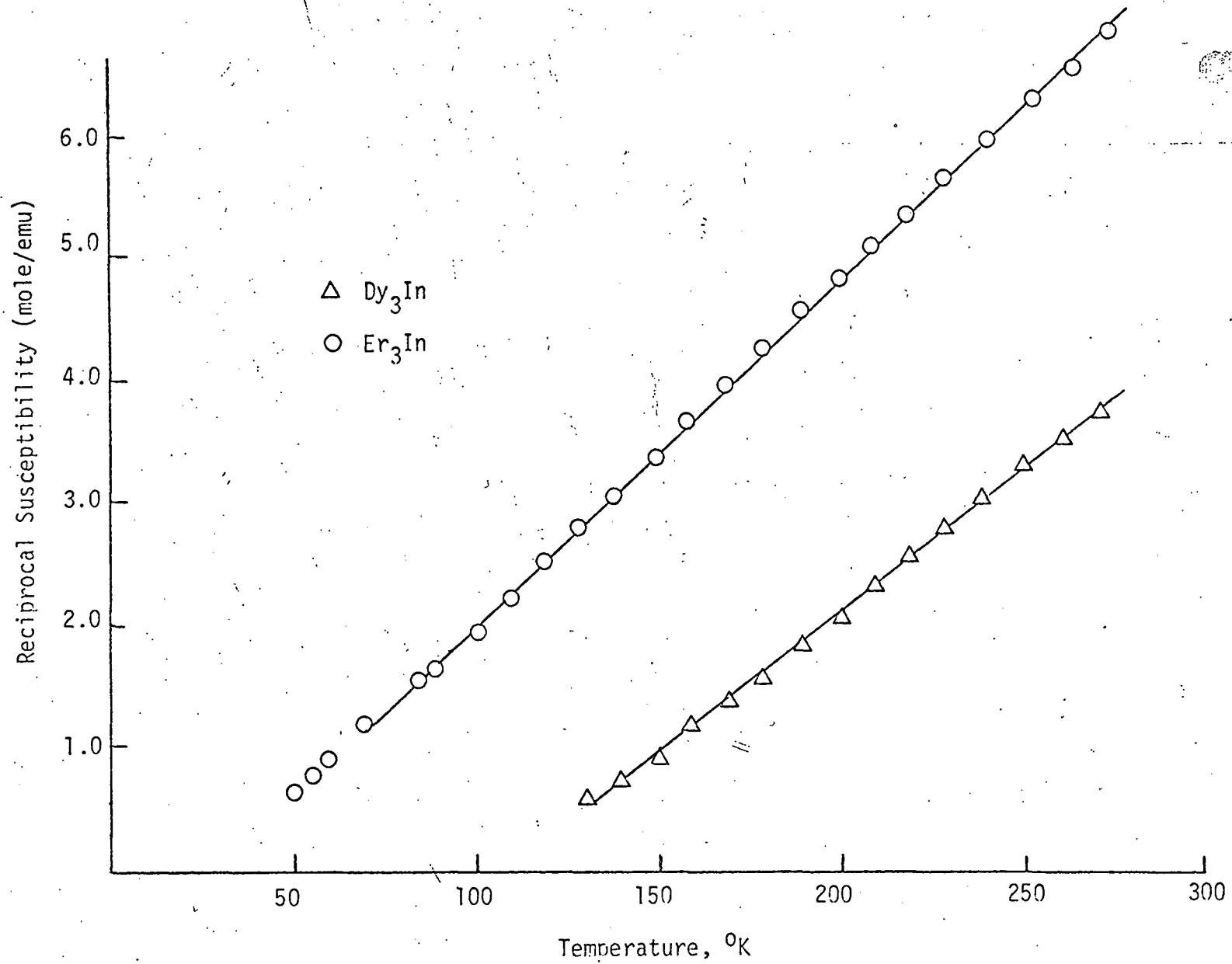
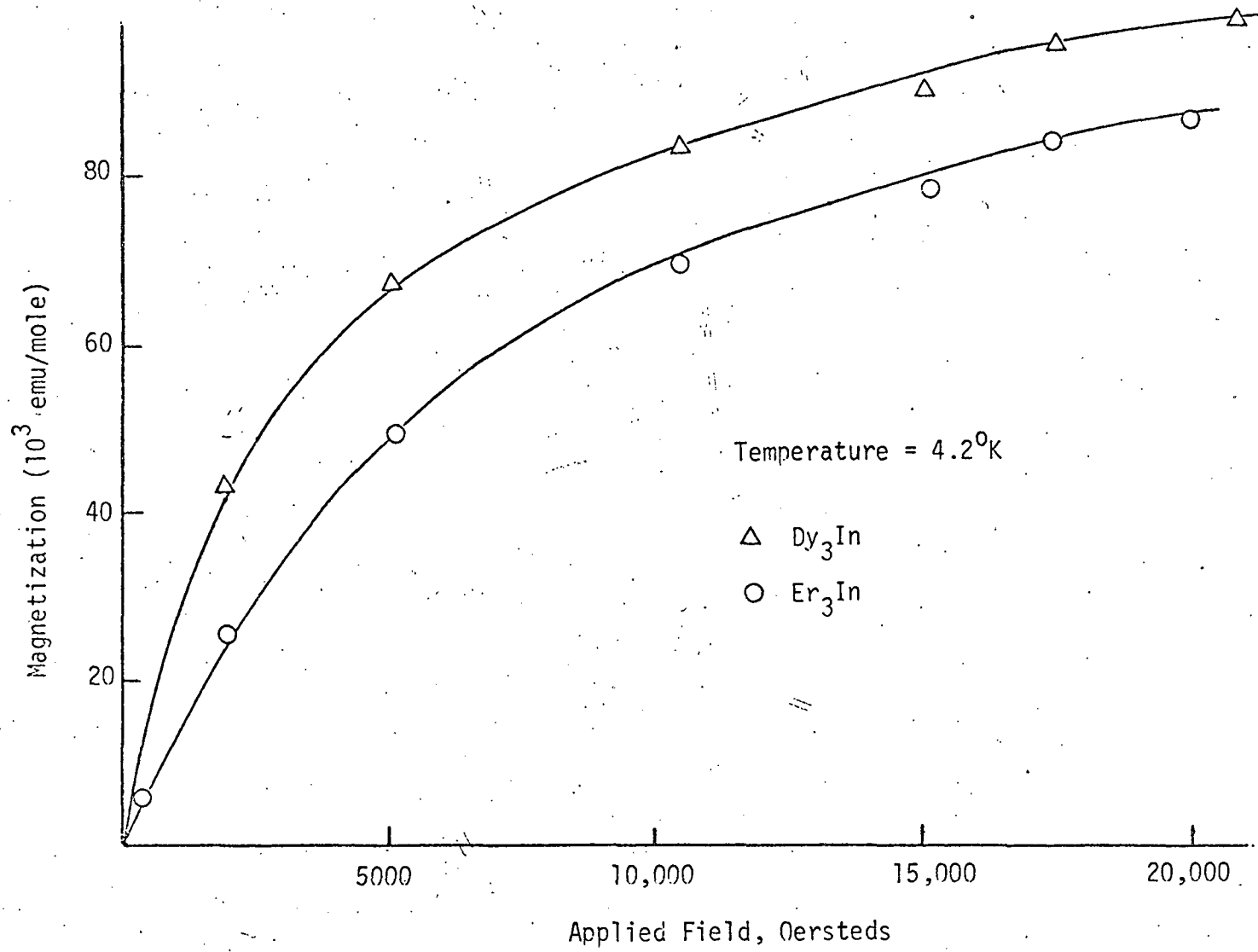


Figure 10 - Reciprocal Susceptibility versus Temperature,  $\text{Dy}_3\text{In}$  and  $\text{Er}_3\text{In}$



Temperature = 4.2°K

△ Dy<sub>3</sub>In  
○ Er<sub>3</sub>In

Figure 11 Magnetization versus Applied Field, Dy<sub>3</sub>In and Er<sub>3</sub>In

TABLE II  
Magnetic Results\* for  $\text{Ln}_3\text{In}$

Compound	$T_c$	$\mu_{\text{eff}}$	$g[J(J+1)]^{1/2}$	$\mu_{\text{or}}$ (H=20 kOe)	$\theta_p$
$\text{Pr}_3\text{In}$	62°K	3.5	3.58	.23	9.3°K
$\text{Nd}_3\text{In}$	114°K	3.4	3.62	.37	10 °K
$\text{Gd}_3\text{In}$	213°K	8.8	7.94	5.2	196 °K
$\text{Dy}_3\text{In}$	138°K	10.4	10.6	5.8	113 °K
$\text{Er}_3\text{In}$	51°K	9.6	9.6	5.1	31 °K

\* Moments ( $\mu_{\text{eff}}$  and  $\mu_{\text{or}}$ ) are given as  $\mu_B$ /rare earth atom.

In all compounds except for  $\text{Gd}_3\text{In}$ , no unusual magnetic behavior was found.  $\text{Pr}_3\text{In}$ ,  $\text{Nd}_3\text{In}$ ,  $\text{Er}_3\text{In}$  and  $\text{Dy}_3\text{In}$  became ferromagnetic with Curie points in the temperature range expected when only rare earth-rare earth interactions are involved. However, it does appear this magnetic order is of the "hard" variety. This means that an extremely high field (~100 kOe) must be applied to achieve complete saturation. The magnetic moment at 20 kOe is only a fraction expected for a rare earth ion (example,  $\text{Er}_3\text{In}$ : 5.1 Bohr magnetons compared to a  $gJ$  value of 9.0 Bohr magnetons).

$\text{Gd}_3\text{In}$  appears to have a complicated magnetic structure. It is possible that the spins are canted. At the lower fields the moments on the Gd atoms oppose each other giving an antiferromagnetic type of ordering. As the field is increased these two moments could align themselves in the direction of the field assuming a ferromagnetic type of order. A neutron diffraction study of this compound would be beneficial in deciding if the spins are canted in zero field as they appear to be from the magnetic results.

## (4) Work in Progress

Heat Capacity Studies of  $\text{LnCo}_5$  Compounds

(work of D. Keller and S. G. Sankar)

In last year's report a second 10 - 300°K calorimeter was mentioned as being prepared for use. It has now been put into operation, after some modification and repair. A new Pt thermometer was installed, most of the low temperature section was revised, the old sample holder was remade, and the thermometer and heater circuits were somewhat modified. After completing the above changes the system was calibrated using benzoic acid from the National Bureau of Standards. The deviations from the standard values averaged ~.2% high from ~20 - 300°K, then increased to ~5% at 10°K.

After calibration, a thermodynamic study was begun on the potentially very useful permanent magnet materials, the rare earth-cobalt 1:5 compounds ( $\text{LnCo}_5$ ). In the past year we have measured the heat capacity from ~4 - 300°K of three of the 1:5 compounds, namely  $\text{PrCo}_5$ ,  $\text{NdCo}_5$  and  $\text{GdCo}_5$ .

These compounds had been studied earlier within our group by thermomagnetic analysis, and later work was done elsewhere using neutron diffraction on  $\text{NdCo}_5$ , and using magnetic anisotropy measurements on  $\text{NdCo}_5$  and  $\text{PrCo}_5$ . The net result of these investigations was to establish that the "easy-axis" of magnetization rotated away from the c-axis toward the basal plane as one lowered the temperature below ~290°K for  $\text{NdCo}_5$  and below ~110°K for  $\text{PrCo}_5$ .

In our heat capacity measurements we have observed anomalies at roughly the temperatures mentioned above for  $\text{NdCo}_5$  and  $\text{PrCo}_5$ . We hope to measure their electronic heat capacities, and to estimate their

X  
no  
data

lattice heat capacities using a suitable isomorph such as  $\text{LaCo}_5$  or  $\text{LaNi}_5$  (which has already been measured in the group), in order to extract the change in enthalpy ( $\Delta H$ ) and the change in entropy ( $\Delta S$ ) associated with these "easy-axis" rotations. These values could then be compared with those predicted by models, such as the phenomenological description given by  $E_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta$ , where  $E_a$  is the anisotropy free energy,  $K_1$  and  $K_2$  are phenomenological constants, and  $\theta$  is the angle of rotation away from the c-axis.

Heat Capacity Studies of  $\text{LnAl}_2$  Compounds  
(work of T. Hill and C. A. Bechman\*)

The study has involved  $\text{LnAl}_2$  compounds with  $\text{Ln} = \text{Tb}, \text{Ho}$  and  $\text{Er}$ . The work on  $\text{HoAl}_2$  has been completed and Figs. 12-14 indicate the results obtained. The Curie temperature has been reported (by magnetic work) to be  $\sim 28^\circ\text{K}$ . However, Fig. 12 indicates that more than a ferro- to paramagnetic transition is taking place, (peaks at both  $19.2$  and  $28.2^\circ\text{K}$ ). The  $C_p$  measurements were run from  $\sim 4.8$  to  $300^\circ\text{K}$  and a  $C_p$  of  $71.8$  (j/mole deg) was obtained at  $300^\circ\text{K}$ .

Plots for the low temperature ( $1.5 - 12^\circ\text{K}$ ) are given in Figs. 13 and 14. Points which are not encircled represent data obtained with the pulse calorimeter which is now under on-line computer control. Encircled points show data obtained with the conventional adiabatic unit, which, since it employs a platinum resistance thermometer, becomes inaccurate below  $10^\circ\text{K}$ . Disparity between results obtained employing the two units is brought out in Figs. 13 and 14.

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\*Dr. Bechman has been supported on a gift by the Gulf Oil Corporation in the furtherance of work on strongly paramagnetic solids.



CP  
[T/M-KO]

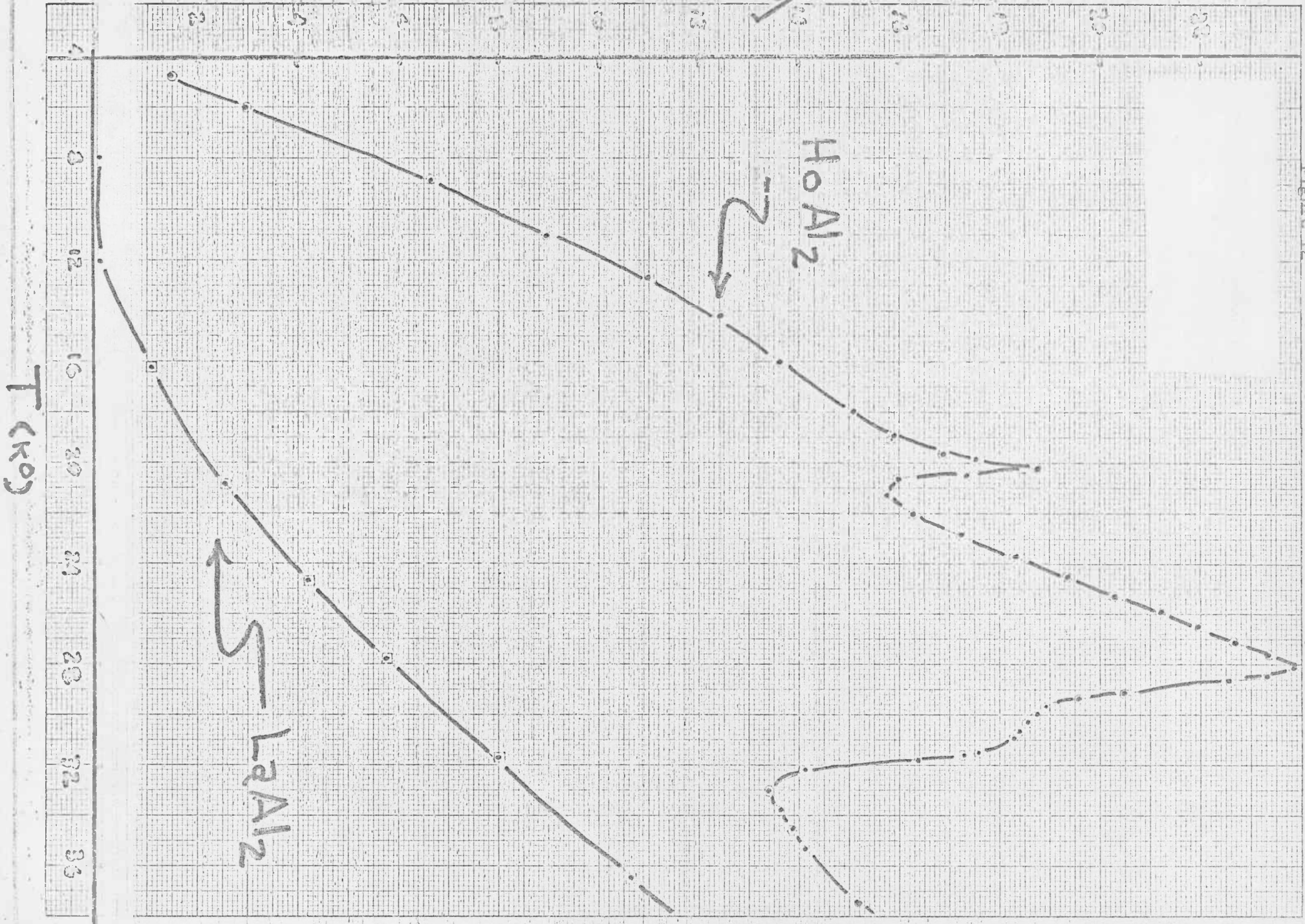


Figure 12

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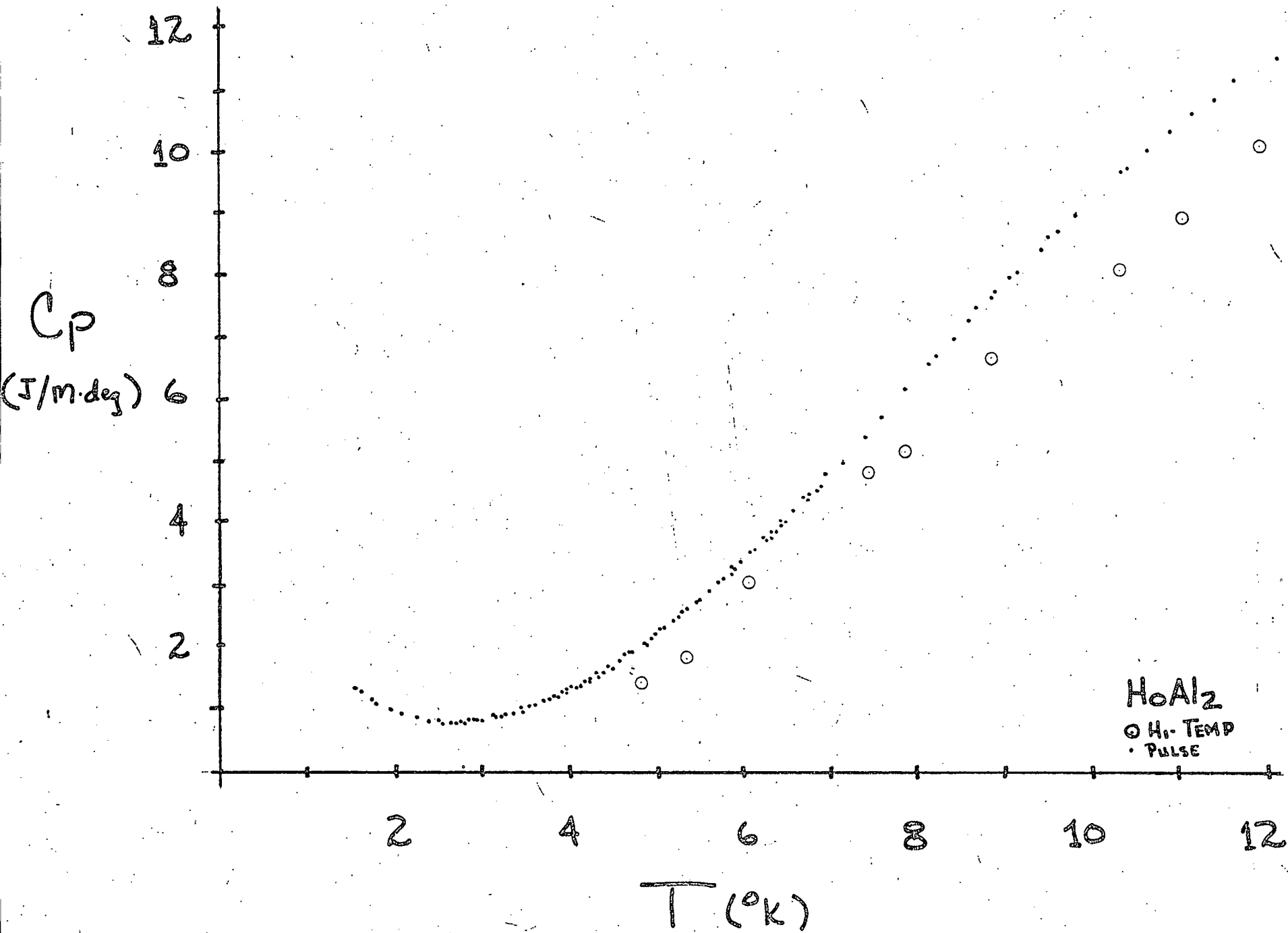


Figure 13



The rise in  $C_p$  below  $2.5^\circ\text{K}$  may be due to the hyperfine interaction.

$\text{ErAl}_2$  has been prepared and will be run in the near future.  $\text{TbAl}_2$  is being prepared at the present time.

Magnetic Studies of Pseudo-binary 1-5 Cobalt Compounds  
(work of T. Swearingen\*)

In the process of studying pseudo-binary systems described in an earlier report, four of these alloys, all of which had rather high magnetic moments, were ground up to below  $50\mu$  marticle size and aligned in a magnetic field of 6000 Oe. These pellets were then compressed with five tons pressure, polished and a hysteresis measurement was performed. The following table lists some properties of these ternaries along with their parent compounds and  $\text{Gd}_{.7}\text{Ca}_{.3}\text{Co}_5$  and the alloy of Yb and Co corresponding to " $\text{YbCo}_5$ " ( $\text{Yb}_2\text{Co}_{17} + \text{YbCo}_3$ ).  $B_r$  was calculated assuming a density of  $8.0 \text{ g/cm}^3$ .

Table III

Magnetic Characteristics of Some 1-5 Cobalt Systems

	Magnetization Direction	$\sigma_s$ (room temp) in $\mu_B$	$B_r$ (gauss)	$\frac{H}{m c}$	$T_c$
$\text{CeCo}_5$	c	5.5		$2800^a, 315^b$	735
$\text{Ho}_{.1}\text{Ce}_{.9}\text{Co}_5$	c	6.8	3600	700	790
$\text{Ho}_{.2}\text{Ce}_{.8}\text{Co}_5$	c	5.9	3600	750	850
$\text{ThCo}_5$	c	4.8		$1990^a$	550
$\text{Ho}_{.1}\text{Th}_{.9}\text{Co}_5$	c	6.1	2600	600	600

\*T. Swearingen was holder of an IBM Predoctoral Fellowship for the nine month academic year. He receives AEC support for the three summer months.

Table III  
(continued)

$\text{Ho}_{.2}\text{Th}_{.8}\text{Co}_5$	c	6.3	3200	700	660
$\text{GdCo}_5$	c	2.6		13,000 <sup>a</sup>	1000
$\text{Gd}_{.7}\text{Ca}_{.3}\text{Co}_5$	c	7.1	3300	700	> 900
" $\text{YbCo}_5$ "	-	112 emu/g	1000	150	> 900

<sup>a</sup>J.J. Becker, J. Appl. Phys. 41, 1055 (1970).

<sup>b</sup>K.H.J. Buschow, J. Appl. Phys. 39, 1717 (1968).

As a continuation of previous work concerned with altering the electron concentration in  $\text{RCo}_5$  (R = Gd, Ho, Er), attempts were made to substitute Ca, Bi and Yb for the rare earth metal. Experiments with Bi were totally unsuccessful and those with Ca questionable as to substitution. Each has an affinity for the rare earth, yet neither shows any willingness for chemical union with Co. When heated, a ternary of the form  $\text{Gd}_{.9}\text{Ca}_{.1}\text{Co}_5$  will release Ca vapor. The saturation moment is somewhat higher than  $\text{GdCo}_5$  as might be expected but there is no evidence to suggest a change in the exchange coupling. On the other hand there is some indication that a small amount of Ca enhances the Curie temperature of  $\text{ThCo}_5$  considerably.

When the substituent was Yb, metallographic examination revealed the existence of two phases in  $\text{Gd}_{1-x}\text{Yb}_x\text{Co}_5$  and three or four phases in  $\text{Ho}_{1-x}\text{Yb}_x\text{Co}_{5+\delta}$  and  $\text{Er}_{1-x}\text{Yb}_x\text{Co}_{5+\delta}$ . Annealing and addition of more Co tended to increase the amount of other phases. It seems even small amounts of Yb addition makes the parent compound unstable. This has been reported

in the literature. Also, no marked change in saturation moments at 4.2°K has been found. This would be predictable if Yb exists in the +3 valence.

#### Studies of Intermetallics Involving Yb and the 3d Transition Metals

The binary systems Yb-Fe, Yb-Co and Yb-Ni are currently being investigated. The several intermetallic compounds between Yb and the above-mentioned transition metals have been identified by means of X-ray diffraction, thermomagnetic analysis and metallographic examination. The values of the lattice parameters and the magnetic data indicate that Yb is trivalent and antiferromagnetically coupled with the transition metal in most, if not all, of the intermetallics in these series.

Table III represents the materials which have been formed to date in this laboratory. The Yb-Ni and Yb-Fe listings are not yet complete. It is also believed that  $\text{Yb}_x\text{Co}$ ,  $\text{Yb}_4\text{Co}_3$  and  $\text{YbCo}_3$  exist, although the high vapor pressure of Yb makes their synthesis difficult.

Table IV

#### Summary of Structural Information for Yb Compounds

Structure	Lattice Symmetries	a	c	T <sub>c</sub>	Magnetic Structure	
Yb <sub>6</sub> Fe <sub>23</sub>	Th <sub>6</sub> Mn <sub>23</sub>	cubic	11.93	-	480	Fo <sup>a</sup>
Yb <sub>2</sub> Fe <sub>17</sub>	Th <sub>2</sub> Ni <sub>17</sub>	hexagonal	8.42	8.25	285	Fo
YbCo <sub>2</sub>	MgCu <sub>2</sub>	cubic	7.10	-	< 77	-
YbCo <sub>3</sub>	PuNi <sub>3</sub>	rhombohedral	4.95	24.11	490	Fo
Yb <sub>2</sub> Co <sub>7</sub> (?)	Ce <sub>2</sub> Ni <sub>7</sub> (?)	hexagonal	4.96	24.23	550	Fo
YbCo <sub>5</sub>	(appears not to exist)					
Yb <sub>2</sub> Co <sub>17</sub>	Th <sub>2</sub> Ni <sub>17</sub>	hexagonal	8.30	8.10	> 900	Fo
YbNi <sub>3</sub>	PuNi <sub>3</sub>	rhombohedral	4.92	24.13	< 77	-

<sup>a</sup>F<sub>0</sub> denotes a ferromagnetic or ferrimagnetic material.

Table IV  
(continued)

(appears not to exist)						
$\text{Yb}_2\text{Ni}_7$						
$\text{YbNi}_5$	$\text{CaZn}_5$	hexagonal	4.85	3.96	< 77	-
$\text{Yb}_2\text{Ni}_{17}$	$\text{Th}_2\text{Ni}_{17}$	hexagonal	8.28	8.02	~ 80	-

So far it appears only Yb in combination with Ni yields single phase materials. Two compounds with stoichiometry near 50 wt. % Co have been detected by a substantial difference in Curie temperature. The structure types, however, are nearly identical. The correct stoichiometries of these have been temporarily assigned  $\text{YbCo}_3$  and  $\text{Yb}_2\text{Co}_7$ , respectively, since their Curie points fit in well with their predicted values obtained from the other heavy rare earth  $\text{RCO}_3$  and  $\text{R}_2\text{Co}_7$  behavior. Annealing of the " $\text{Yb}_2\text{Co}_7$ " below  $1200^\circ\text{C}$  for a short period of time converts it to the other form.

$\text{Yb}_2\text{Co}_{17}$  can be made in 90% purity. Its saturation moment at room temperature is over  $20\mu_B$  and the c crystallographic axis is the favored direction. Unfortunately, the anisotropy field,  $H_A$ , is little more than 10 kOe.

Magnetic Studies of the  $\text{Gd}_{1-x}\text{Ce}_x\text{Fe}_2$  and  $\text{Gd}_{1-x}\text{Th}_x\text{Fe}_2$  Systems  
(work of E. Miskinis)

$\text{GdFe}_2$  is a ferrimagnetic material. In an effort to change the coupling by modification of the electron concentration a portion of tripositive Gd is replaced with quadripesitive Ce or Th. Experiment showed that the coupling remains antiferromagnetic. The behavior resembles

that observed<sup>4</sup> by Shidlovsky and Wallace in this laboratory several years ago for  $\text{Ln}_{1-x}\text{Zr}_x\text{Fe}_2$  with Ln = Gd, Dy and Ho.

The Fe moment estimated from the measured magnetization at 4°K (assuming antiparallel coupling) is given in Table V. One sees that substantial replacement of Gd with either Ce or Th leads to a decrease in Fe moment.

Table V

Fe Moment in  $\text{Gd}_{1-x}\text{Ce}_x\text{Fe}_2$  and  $\text{Gd}_{1-x}\text{Th}_x\text{Fe}_2$ 

	Fe Moment ( $\mu_B$ )		Fe Moment ( $\mu_B$ )
$\text{GdFe}_2$	1.87	$\text{Gd}_{.8}\text{Ce}_{.2}\text{Fe}_2$	1.92
$\text{Gd}_{.95}\text{Th}_{.05}\text{Fe}_2$	1.93	$\text{Gd}_{.6}\text{Ce}_{.4}\text{Fe}_2$	1.73
$\text{Gd}_{.9}\text{Th}_{.1}\text{Fe}_2$	1.88	$\text{Gd}_{.2}\text{Ce}_{.8}\text{Fe}_2$	1.64
$\text{Gd}_{.8}\text{Th}_{.2}\text{Fe}_2$	1.82	$\text{CeFe}_2$	1.13
$\text{Gd}_{.6}\text{Th}_{.4}\text{Fe}_2$	0.72		

It appears that the increased electron concentration results in filling of the d-band and loss of Fe moment, as was observed in the several systems studied by Shidlovsky and Wallace. The hoped-for coupling reversal did not occur, perhaps because the electron concentration actually did not increase. The extra electrons provided by Ce or Th are absorbed by Fe.

<sup>4</sup>I. Shidlovsky and W.E. Wallace, J. Sol. State Chem. 2, 193 (1970).



Hydrogen Removal Under Ultrahigh Vacuum Conditions  
and the Effect on Physical Properties  
(Primarily the work of C.G. Titcomb)

The report covering the period 1970-1 described the general procedure employed in degassing rare earth intermetallic compounds and the preliminary results obtained to that time. The resistivity of fourteen compounds chosen at random had been examined before and after degassing and their behavior had been found to divide into three main types, each of which was described. The work proposed for the following year was to extend these exploratory resistivity measurements to a still wider selection of compounds, identify the desorbed gas, and then make detailed studies of compounds whose behavior seemed especially significant with other types of measurements.

To assist the survey of compounds by resistivity measurements, the equipment was modified to enable it to be coupled to an on-line computer. The associated program permitted the computer simultaneously to control the experiments, execute the necessary calculations and record the final data. Automatic control led to at least a threefold increase in the speed at which specimens could be examined and a substantial increase in precision. During development and refinement of the computer program, precise determinations were made of the resistivity-temperature behavior of the series of compounds  $RNi_5$  ( $R = La, Ce, Pr, Nd, Gd, Dy$  and  $Ho$ ). The use of the equipment in connection with present degassing work is now largely passed but it is used by other investigators in studies of spin disorder resistivity in rare earth intermetallics, of the Kondo effect and superconductivity.

Mass spectroscopy confirmed the identification of the main constituent of the desorbed gas as hydrogen.

The shapes of the resistivity-temperature curves for  $\text{PrCo}_2$  and  $\text{NdCo}_2$ , as described in the previous report, were radically altered by sample degassing. That significant changes had been effected in the materials was confirmed by magnetic and X-ray measurements. The forms of the susceptibility-temperature curves in the range 0 - 300°K are also grossly changed and the parameters of the (cubic) lattice structures are reduced by ~1.9% (see paper No. 14 in section II-B-1). Recently, measurements have been commenced on the compounds  $\text{GdCo}_2$ ,  $\text{DyCo}_2$  and  $\text{HoCo}_2$  to see how far this behavior is typical of other members of the series.  $\text{GdCo}_2$  and  $\text{DyCo}_2$  show lattice parameter reductions of about the same size.

$\text{Ln}_{1-x}\text{Ln}'_x\text{Co}_5$  compounds ( $\text{Ln}, \text{Ln}' = \text{Ce}, \text{Y}; \text{La}, \text{Y}; \text{Pr}, \text{Y}; \text{Ce}, \text{La}; \text{Pr}, \text{La}; 0 \leq x \leq 1$ ) were prepared by induction melting of stoichiometric proportions of the component elements in a cold boat followed by an initial annealing period of seven days at 950°C. X-ray diffraction measurements showed that each compound possessed the hexagonal  $\text{CaCu}_5$  structure with lattice parameters a and c as given in Table VI. Both parameters vary linearly across each series showing that at every composition a single-phase material is formed, a condition confirmed by metallography. No difficulty was experienced in making the specimens except  $\text{LaCo}_5$  and those containing relatively large proportions of La ( $\text{La}_{.8}\text{Ce}_{.2}\text{Co}_5$ , etc.).  $\text{LaCo}_5$ , after the standard annealing period, appeared to contain about 20% of a second phase while the other materials frequently possessed three phases. Further annealing under the same conditions (samples sealed in glass capsules evacuated to  $\sim 10^{-3}$  Torr) produced no noticeable improvements. Heating these multiphasic specimens under ultrahigh vacuum (u.h.v.) conditions at 1000°C for two days, however, effectively eliminated the extraneous

Table VI

Lattice Parameters, Curie Points and Room Temperature Magnetizations  
of Compounds in the Series  $R_{1-x}R'Co_5$

Compound	$\underline{a}$ (Å)	$\underline{c}$ (Å)	$T_c$ (K)	$\mu_T$ (6 kOe.) ( $\mu_B$ /f.u.)
CeCo <sub>5</sub>	4.922	4.008	734	4.71
Ce <sub>.8</sub> Y <sub>.2</sub> Co <sub>5</sub>	4.925	4.010	770	5.44
Ce <sub>.6</sub> Y <sub>.4</sub> Co <sub>5</sub>	4.924	4.005	810	6.36
Ce <sub>.4</sub> Y <sub>.6</sub> Co <sub>5</sub>	4.932	3.992	840	6.82
Ce <sub>.2</sub> Y <sub>.8</sub> Co <sub>5</sub>	4.936	3.985	887	7.05
YCo <sub>5</sub>	4.946	3.975	936	6.69
LaCo <sub>5</sub>	5.105	3.967	842	4.70
La <sub>.8</sub> Y <sub>.2</sub> Co <sub>5</sub>	5.069	3.968	860	4.63
La <sub>.6</sub> Y <sub>.4</sub> Co <sub>5</sub>	5.033	3.974	876	4.36
La <sub>.4</sub> Y <sub>.6</sub> Co <sub>5</sub>	5.000	3.971	895	4.45
La <sub>.2</sub> Y <sub>.8</sub> Co <sub>5</sub>	4.970	3.970	917	5.12
PrCo <sub>5</sub>	5.018	3.982	909	5.97
Pr <sub>.8</sub> Y <sub>.2</sub> Co <sub>5</sub>	4.998	3.982	916	5.77
Pr <sub>.6</sub> Y <sub>.4</sub> Co <sub>5</sub>	4.982	3.978	918	5.08
Pr <sub>.4</sub> Y <sub>.6</sub> Co <sub>5</sub>	4.970	3.973	924	4.89
Pr <sub>.2</sub> Y <sub>.8</sub> Co <sub>5</sub>	4.950	3.970	928	4.75

Table VI  
(continued)

$\text{Ce}_{.8}\text{La}_{.2}\text{Co}_5$	4.951	4.009	756	3.82
$\text{Ce}_{.6}\text{La}_{.4}\text{Co}_5$	4.980	4.010	769	3.42
$\text{Ce}_{.4}\text{La}_{.6}\text{Co}_5$	5.015	3.999	800	3.46
$\text{Ce}_{.2}\text{La}_{.8}\text{Co}_5$	5.054	3.987	815	3.79
$\text{La}_{.8}\text{Pr}_{.2}\text{Co}_5$	5.064	3.965	848	4.18
$\text{La}_{.6}\text{Pr}_{.4}\text{Co}_5$	5.059	3.970	863	4.12
$\text{La}_{.4}\text{Pr}_{.6}\text{Co}_5$	5.042	3.974	879	4.17
$\text{La}_{.2}\text{Pr}_{.8}\text{Co}_5$	5.030	3.976	893	4.45

phases from the  $\text{La}_{.8}$  compounds and reduced the amount of second phase in  $\text{LaCo}_5$  to half its previous value. A further six days' annealing under the same conditions reduced the second phase in  $\text{LaCo}_5$  to small and probably insignificant traces along the grain boundaries. The compounds for which u.h.v. annealing was required appeared to be unstable, however. The exertion of stress on the material (for example, in crushing and grinding to a powder) generally led to the reappearance of the other phases. For this reason magnetic measurements (see below) on these samples were performed using small uncrushed pieces of material. In addition to reducing the secondary phases, u.h.v. annealing diminished the  $c$  lattice parameters of the materials by  $\sim 1/2\%$ ; the  $a$  parameters remained constant.

The magnetization of the compounds in a field of 6 kOe was measured as a function of temperature in the range 300 - 1000°K. All materials exhibited normal ferromagnetic behavior; values of the Curie points,  $T_c$  and the room temperature magnetic moments,  $\mu_T$ , are given in the table. As expected,  $T_c$  also varied linearly across each series. The Curie points for the end compounds ( $\text{CeCo}_5$ ,  $\text{PrCo}_5$ , etc.) agree well with literature values except in the case of  $\text{YCo}_5$  (experiment - 936°K; literature - 977°K). However, since the value gained in the present work is in accord with the trend exhibited by the neighboring alloys, the literature value is probably too high.

The magnetizations of initially single-phase materials before and after degassing have not yet been measured, but it was found that the u.h.v. annealing process increased the moment per formula unit of " $\text{LaCo}_5$ " from 4.35 to 4.7  $\mu_B$ . The change in  $T_c$  was small (846 - 842°K).

Attempts to broaden the hysteresis loops of pellets of compressed powders of  $\text{In}_{1-x}\text{In}'_x\text{Co}_5$  compounds by degassing in u.h.v. have so far proved unsuccessful, probably due to sintering of the particles. In future experiments lower temperatures will be used.

For a number of intermetallic compounds ( $\text{DyNi}_3$ ,  $\text{DyCoNi}_2$ ,  $\text{TbAl}_2$ ), degassing has been found to produce significant changes in the low temperature heat capacities. The overall values of the heat capacities are generally reduced (sometimes by as much as 15%) and certain peaks (now thought to be due to hydroxides) are eliminated. However, occasionally the lowering of the heat capacity curve uncovers further large and well defined peaks that were previously unsuspected. It is hoped that more general use of u.h.v. degassing will make heat capacity data obtained in this laboratory easier to interpret and result in more meaningful values of lattice and electronic specific heats.

#### Ultrahigh Vacuum Guage Calibration

(work of C.G. Titcomb)

In connection with the work described above, in which it was desirable to estimate the quantities of gas being desorbed from the specimens, a new and simple method of calibrating u.h.v. ionization gauges was developed. The essential features of the technique are described in paper No. 16 in Section II-B-1. The accurate measurement of reduced pressures is a critical need in many fields of technology. Yet hitherto workers have been forced to use instruments lacking dependable calibrations because of the difficulties in setting up reliable pressure standards, despite much research into the subject. It is hoped the proposed method will go a long way towards solving this problem.

III. Percentage of Effort by Principal Investigators

A. Period September 1, 1971 - May 30, 1972

W.E. Wallace - 30%

R.S. Craig - 40%

B. Period June 1, 1972 - August 31, 1972

W.E. Wallace - 40%

R.S. Craig - 40%

## APPENDIX I

Published Work Since Inception of Program

## A. Work Published Prior to 1964

In the interest of brevity these are not cited in detail. They total 56 publications. A complete list of these may be found in the Annual Report submitted on May 15, 1965, report number NYO-3454-1.

## B. Work Published 1964 to Present

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